# SOILS AND THE GLOBAL CARBON CYCLE<sup>1</sup>

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#### INTRODUCTION

Organic matter plays a key role in determining most soil properties. Historically, the focus of research on soil carbon has been the central role that organic matter plays in determining soil fertility. This chapter will focus on a more recent interest, the role of soil organic carbon in the global carbon cycle.

Soil organic matter (SOM) is one of the largest carbon reservoirs that is in rapid exchange with atmospheric CO<sub>2</sub>, and it is thus important as a potential source and sink of the greenhouse gas over time scales of human concern (Schimel, 1995). It is also an important human resource and a C reservoir that is under active management in agricultural and range lands worldwide. Questions driving present research on the soil C cycle include: Are soils now acting as a net source or sink of carbon to the atmosphere? What role will soils play as a natural modulator or amplifier of climatic warming? What role will soil management play in international policies controlling emissions of CO<sub>2</sub> and other trace gases in the coming century? How will these natural and policy changes affect the productivity of agricultural and other ecosystems? Answering these questions will require a mechanistic understanding of how and why C is stored in soils.

We review here the most important factors controlling the distribution and dynamics of SOM across landscapes, and the methods used to study rates of exchange between atmospheric CO<sub>2</sub> and SOM. An appendix details the use of a relatively new isotopic tool, radiocarbon (<sup>14</sup>C), to study SOM dynamics. We will mention some of the hypotheses under current discussion regarding future responses of soil carbon to global environmental change. However, definitive answers to the questions do not yet exist.

### **Inorganic Carbon in Soils**

Carbon is stored in soils both in organic and inorganic forms. While we will focus here on organic forms, interactions between atmospheric CO<sub>2</sub> and inorganic components of soils through weathering and carbonate precipitation and dissolution are important regulators of atmospheric CO<sub>2</sub> on very long time scales (Berner et al., 1983). The present rate of CO<sub>2</sub> consumption during weathering is estimated presently at about 0.4 Pg C/y globally (Holmen, 1992). Weathering rates,

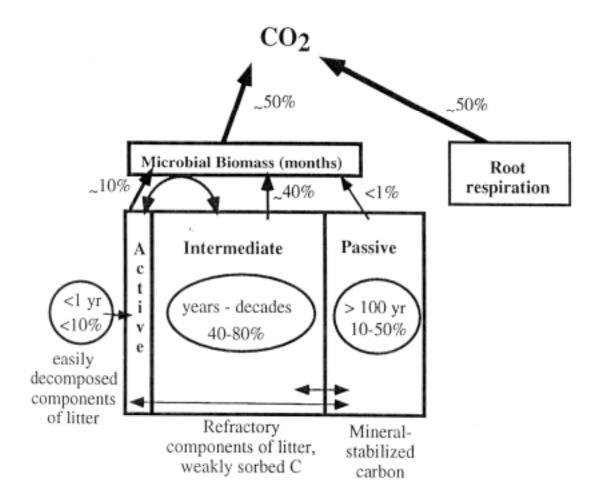
<sup>&</sup>lt;sup>1</sup> This document was originally prepared as a book chapter for the 1997 NATO Advanced Study Institute "Soils and Global Change." Please cite as: Trumbore, S.E. and M.S. Torn. Soils and the Global Carbon Cycle. In EA Holland, ed. Soils and Global Change, NATO Advanced Study Institute, in press; LBNL-44910, 2003. <a href="http://esd.lbl.gov/ESD">http://esd.lbl.gov/ESD</a> staff/torn/nato soilcarbon.pdf.

and therefore CO<sub>2</sub> consumption, have been shown to vary locally with the stage of soil development (Chadwick et al., 1994) and globally with the fraction of young crust exposed for weathering (Harden et al., 1992). On very long time scales, rates of C consumption by weathering are less than or equal to rates of sequestration of organic C on the new minerals being formed in soils (Chadwick et al., 1994; FranceLanord and Derry, 1997).

Pedogenic carbonates are formed when dissolved bicarbonate formed by weathering precipitates in the soil. They form in arid and semi-arid regions, where local evaporation exceeds precipitation. They also form in humid climates when dissolved bicarbonate moves vertically or laterally through the soil. Whether or not pedogenic carbonates represent a net sink for atmospheric CO<sub>2</sub> depends on the source of Ca in the precipitated CaCO<sub>3</sub>. If the Ca is derived from primary silicate minerals, CaCO<sub>3</sub> precipitation is a net sink. However, in some cases, the Ca source is from dissolution of limestone or dolomite, in which case pedogenic carbonates merely translocate C within the soil profile but are not a net sink of atmospheric C. Because they build up slowly and are stable over millennia, pedogenic carbonates are not thought to play a major role in the short-term carbon cycle (Schlesinger, 1997). The total amount of carbonate C stored to 1 m depth is estimated at 695–748 Pg of C (Batjes, 1996).

### **Organic Carbon**

An overall picture of C cycling in SOM is shown in Figure 1. The initial source of organic matter in soils is fixation of atmospheric CO<sub>2</sub> by plant photosynthesis. When the plant senesces or dies, its organic material is added to the soil. The activity of soil fauna (especially fungi and microbial communities) metabolizes some of these substrates and transforms others into more resistant organic compounds (collectively referred to as humus). As we define it here, the term "soil organic matter" (or "SOM") includes all the dead organic compounds in soil, in all states of decay, ranging from fresh dead plant litter, to microbial cell walls, to humic materials stabilized on mineral surfaces. The main loss pathway of organic carbon from soils is decomposition to CO<sub>2</sub>, although leaching or erosion is significant in some sites and on long time scales. The decomposition rate, or its inverse, turnover time, of SOM varies widely. Turnover times of organic matter in soils range from hours for highly decomposable sugars exuded by roots, to >100,000 years for C associated with noncrystalline minerals (Torn et al., 1997). This extreme heterogeneity in chemical form and behavior is responsible for much of the difficulty in studying SOM.



**Figure 1.** Schematic overview of C cycling in soils.

#### The Amount of C Stored in Soils

The amount of organic carbon stored in a soil profile is calculated from measurement of both the bulk density (BD) and the mass fraction of C in soil material:

C inventory 
$$\left(\frac{g\ C}{cm^2}\right) = \sum_{all\ horizons}$$
 Bulk Density  $\left(\frac{g}{cm^3}\right) \times \left(\frac{g\ C}{g\ soil}\right) \times$  depth  $(cm) \times (1-fraction\ gravel)$ 

The last term is a correction for stones and gravel greater than 2 mm in size. The largest uncertainties in determining C inventory usually come from estimates of bulk density (the oven-dry weight of a known volume of soil) and the volume of soil that is gravel. It is difficult to collect a precise volume of soil, and in many studies bulk density simply hasn't been measured at all. Large plant fragments and organic mats are often excluded from the estimates of C in soil, either during sample collection or during sieving at 2 mm.

Making a global estimate of the amount of C stored in soils requires extrapolating measurements of C inventory for individual soil profiles to larger regions. To construct the basis for this extrapolation, we need to look for ways to link soil C to factors that are mapped globally.

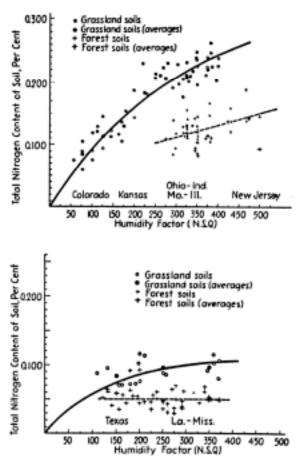
Are there predictable ways in which C storage varies across the landscape? Jenny (1941), expanding on an approach by Dokuchaev (Glinka, 1927; Jenny, 1941), suggested that soil properties, including C inventory, may be predicted from soil forming factors. This is expressed as the "clorpt" equation:

Soil property (in this case, C inventory) = f(cl,o,r,p,t),

where cl = climate, o = potential organisms (vegetation + soil fauna), r = relief (aspect and topography) p = parent material, and t = time. While this may seem to be only common sense, the most important contribution by Jenny was the experimental approach that derives from the clorpt relation (Amundson and Jenny, 1997). To understand or quantify the effect of one variable (for example, time), one can locate a series of sites with the same climate, vegetation, and parent material, but different soil age. Figures 2, 3, and 4 show examples of the influence of three soil-forming factors on C storage.

#### Climate

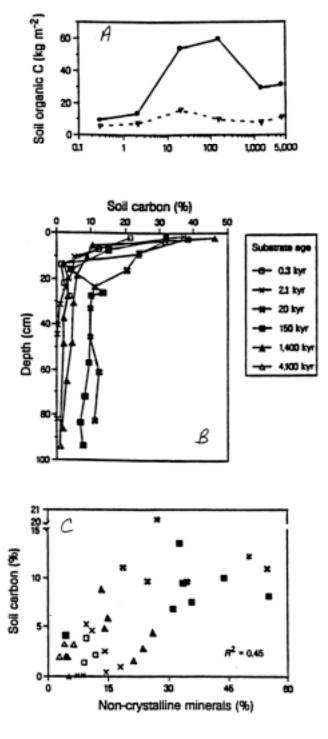
Figure 2 shows how C storage varies in soil sampled across the U.S. Great Plains region. Here, the parent material consists largely of loess deposited during the last glacial period. Precipitation varies longitudinally, with rainfall increasing west-to-east. Mean annual temperature varies latitudinally, warmest in the south and coldest in the north. Jenny used this region to explore the controls of both temperature and moisture on C inventory. Carbon stocks are largest toward the cooler and wetter northeast, and are smallest in the hotter and drier southwest (from Jenny, 1941).



**Figure 2**. (A, Top Panel) Variations in %N (proportional to C content) with precipitation along the 11°C isotherm in the Great Plains area. The humidity factor (NSQ, or Meyer's quotient), is the total annual precipitation (in millimeters) divided by the absolute saturation deficit of air (mm of mercury). Soils are all developed on loess deposits. (B, Bottom Panel) Change in %N with precipitation along the 19°C isotherm. Note the lower amounts of C at higher mean annual temperature. Source: Jenny, 1994

#### Time

Chronosequences are series of sites with the same climate and parent material but with different substrate or soil ages. They are often constructed from terraces developed from coastal uplift or by rivers. Figure 3 shows how C storage changes along a chronosequence developed on lava and ash deposits of different age in the Hawaiian island chain. They illustrate the general trends seen in many chronosequence studies. C accumulates for the first several-hundred-thousand years of soil development, and declines in very old soils (>several million years). The increase and decline of C has been linked to changes in the amount and type of soil minerals that can stabilize SOM (e.g., Oades, 1988; Torn et al., 1997). In the example from Hawaii, changes in soil C are linked to changes in the amount of noncrystalline secondary minerals like allophane and imogolite, which have large surface areas (Torn et al., 1997). Estimates of C storage in very old soils are complicated by the fact that they are often very deep (tens of meters). Hence, very low C content throughout the profile may still add up to a large amount of stored carbon in the total profile (Sombroek et al., 1993).



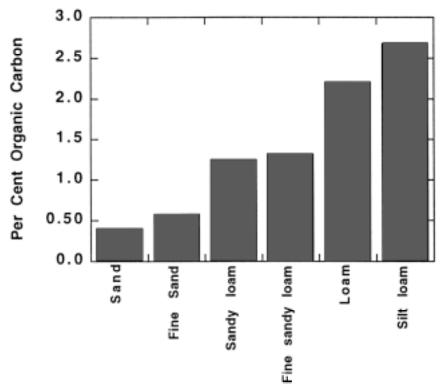
**Figure 3**. Changes in C storage and mineral content along a chronosequence in Hawaii. The parent material is basaltic ash deposits of known age. Climate and vegetation are constant across the sites. A (top) shows the C inventory in SOM versus the age of the parent material. The solid line is the mineral soil C, the dashed line is the O horizon C. The increase and subsequent decrease in SOM is mostly due to changes in the mineral soil. B (middle) shows the distribution of C with depth for the same sites. C (bottom) shows the correlation of soil carbon in mineral horizons with the amount of non-crystalline minerals. Source: Torn et al., 1997.

#### Parent Material

Soils developed on volcanic ash or rocks of basic pH usually contain more organic carbon than those formed on granitic or acidic parent material. Soil texture also has an effect on C storage, even when the composition of the parent material is similar. Figure 4 illustrates this by comparing C inventory in soils developed on postglacial till deposits with different amounts of loess mixed in (Jenny, 1980). Differences in C storage may be linked to differences in the amount and type of secondary soil minerals, as minerals differ in how well they stabilize organic carbon through chemical or physical interactions. In many cases, differences in C storage between soils developed on different parent materials decrease as soils reach great age (millions of years). We speculate that over millions of years, the mineral and associated organic content of different soils tends to converge to a state predicted or constrained by climate.

#### Vegetation

Vegetation controls C storage in two ways. The net primary productivity of vegetation will determine the rate of C inputs to SOM. Thus, for soils where decomposition rates of organic matter are similar, the soils with more productive vegetation will have higher organic C inventory. Losses of C inventory on conversion of forest soils to pasture or agriculture have been attributed to a decrease in vegetation productivity (Trumbore et al., 1995). Vegetation also controls the structure and therefore decomposability of organic matter added to soils. For example, decomposition rates have been linked to the amounts of lignin and nitrogen in plant debris (Melillo et al., 1982). Quideau et al. (1998) show that for a site where parent material, time of soil development, and climate are the same, the amount of C stored varies several-fold, depending on the type of vegetation.



**Figure 4.** Variation of % organic carbon with texture of surface soils developed on glacial till and loess in Iowa (data are from Brown, 1936, as reported in Jenny, 1941).

#### *Topography*

For landscape-scale studies, factors like local topography and soil drainage are important in determining soil C storage. C inventories are higher at the bottom of slopes, in part because erosion transports minerals and associated organic matter formed higher up the slope downward, and also because wetter conditions at the bottom of slopes promote plant productivity and/or inhibit decomposition rates. These landscape-scale variations are particularly important when considering how representative a single soil profile is of regional soil C storage (Davidson and Lefebvre, 1993).

These illustrations give us general rules for predicting how C inventory in soils will vary across large regions and over long time scales. The largest C inventory should be in wet, cool climates, with high ecosystem productivity, on young volcanic surfaces (as in the Pacific Northwest of the USA). The least C should be found in hot, arid regions of low productivity (as in desert soils). Another observation put forth by Jenny is that the form C takes in soils changes with latitude: at low latitudes, very little of the total soil C is stored in surface detritus, and most of the C is associated with the mineral soil. At high latitudes, slow decomposition rates lead to large accumulations of detrital organic material, and relatively little of the organic matter is associated with the mineral soil.

The approach of studying gradients is not without drawbacks. In many regions, clean natural gradients do not exist. One of the problems in climate-gradient studies is that climate and

vegetation cannot always be separated as independent variables across landscapes. Also, the vegetation/climate/soil characteristics in undisturbed ecosystems used for gradient studies represent linkages that have co-evolved over relatively long time scales. The response to sudden disturbance may not necessarily be in the same direction or even magnitude as the response predicted from the gradient. For example, the difference in carbon stock between two sites on the same mountain, one 3°C warmer than the other due to being lower in elevation, may not provide an adequate representation of the change in carbon stock that would occur with a 3°C warming over the course of a century. This is a general weakness in using equilibrium conditions to predict transient responses.

### **Empirical Estimates of Global C Stocks in Soils**

Estimates of the amount of C stored in soils vary from ~800 Pg C to 2,300 Pg C, with recent estimates converging on the range of 1,300–1,600 Pg C. Two approaches have been taken towards estimating the global soil C inventory from existing soil profile data. The first, used by Post et al. (1982) and Schlesinger (1977), relates C storage to climate and vegetation (expressed as Holdridge life zone classification). Post et al. (1982), using climate/vegetation relations developed from 2,700 soil profiles, calculated the global C inventory to be 1,395 Pg C in the top 1 m of soils. A second approach uses soil mapping units in the FAO classification for extrapolation (Eswaran et al., 1993; Batjes, 1996). Soil classification schemes often incorporate information about soil-forming factors such as climate (e.g., "xeric," "cryic") and even parent material (in the case of Andisols). Eswaran (1993) determined the average C inventory to one meter depth for each soil order, based on data from ~1,000 pedons from FAO/UNESCO and 15,000 profiles from the U.S. Dept. of Agriculture databases. The FAO map-based estimate of soil C inventory globally is 1,576 Pg C. Batjes (1996), using a larger soil profile database of 4.353 profiles considered to be representative of soil units on the FAO map, estimates 1,462 to 1,548 Pg of organic C in soils to 1 m depth.

Uncertainties in the global soil C inventory are large. Post et al. (1982) estimate an error of ±200 Pg C (14%), reflecting the variability in soil C inventory within each life zone category. Eswaran et al. (1993) show large coefficients of variation (from 28–70%) for soils within given soil classification categories. Profile data employed for these estimates often use bulk density values estimated from empirical relationships between C content and bulk density, developed from profiles where both were measured (Zinke et al., 1982). These estimates of global C inventory are underestimates, because they do not include important reservoirs of nonliving organic matter present in soils. All omit C stored in surface detritus, which adds an additional 50–200 Pg C (Matthews, 1997). Global extrapolations also do not include estimates of soil C below 1 m; deep soils contain as much C below 1 m as they do above 1 m in some tropical soils (Nepstad et al., 1994) and Histosols (Eswaran et al., 1993). Batjes (1996) estimates an additional ~900 Pg of C stored between 1 and 2 m depth in soils globally. Dead roots that do not pass through a 2 mm sieve are also excluded from estimates of SOM inventory.

### DYNAMICS OF SOIL ORGANIC MATTER

Simply knowing the amount of carbon stored as SOM does not give much insight into the importance of the soil C reservoir for influencing atmospheric CO<sub>2</sub>. For example, if most C in soils is extremely stable, the time for the soil C reservoir to respond to a change in climate or C inputs could be quite long. On time scales greater than a century up to hundreds of thousands of years, changes in ocean C (a much larger C reservoir) may swamp those associated with soils. Therefore, the time scale of interest for studying how soils may influence atmospheric CO<sub>2</sub> is generally less than a century or greater than a million years.

As shown in Figure 1, the most important loss mechanism for C added to soils is through decomposition. The fate of organic matter residues is affected by climate, the quality of the original plant substrate, and the physical environment in the soil (through factors such as temperature, moisture and  $O_2$  availability, and soil mineralogy and structure). SOM is a complex mixture of compounds that decompose on vastly different time scales. A major challenge in determining how long C resides in soils is in identifying components with different turnover times, and understanding how vegetation and soil conditions interact to determine the rate of organic matter decomposition. This section summarizes the observational constraints used to determine C dynamics in soils.

Several terms are used to describe the dynamic cycling of biogeochemical reservoirs. Rodhe (1992) identifies three key terms for expressing dynamics of cycling for a geochemical reservoir. Since we use different observational tools to determine C dynamics, it is important to understand the distinctions among these terms. For a reservoir at steady state (neither gaining nor losing C over time), the **turnover time** ( $\tau_0$ ) is calculated as the inventory (here, the mass of carbon in SOM) divided by the total flux of C out of the reservoir (including decomposition to CO<sub>2</sub>, and transport of dissolved organic or inorganic C out of the soil):

$$\tau_o = \frac{M}{S}$$

The **residence time**  $(\tau_r)$  is the time spent in the reservoir by an individual C atom, which is equivalent to the average age of a molecule leaving the reservoir (assuming its age was 0 when it entered the reservoir):

$$\tau_r = \int_0^\infty \tau \phi(\tau) d\tau$$
, where  $\phi$  = probability density function of residence times of elements in reservoir

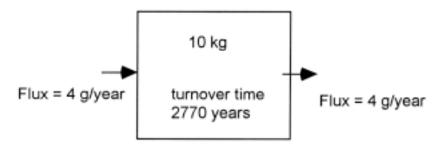
Finally, the **average age** ( $\tau_a$ ) of C atoms in the soil organic matter reservoir is the average time since the atoms entered (whether they are leaving or not):

$$\tau_a = \int_0^\infty \tau \psi(\tau) d\tau$$
, where  $\psi$  = probability density function of ages of elements in reservoir

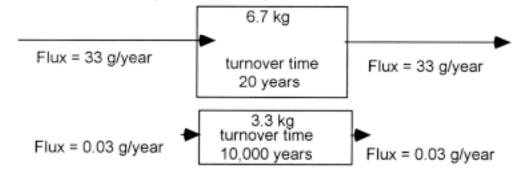
For a homogeneous reservoir (one for which the probability of every atom leaving is equal) at steady state, the turnover time, residence time and average age of organic matter in the reservoir are equal ( $\tau_0 = \tau_r = \tau_a$ ). SOM, however, is a heterogeneous mix of compounds, some that

decompose in hours to years and some that are stable over millennia. As a result, the average age of C atoms in the bulk organic matter reservoir (as measured by radiocarbon) is often greater than the average age of exiting C (the turnover time), as shown in Figure 5. For example, Raich and Schlesinger (1992) calculated the turnover time for C in soils using C inventory (to 1 m depth, and including surface litter) divided by the  $CO_2$  emission observed for the same ecosystem (corrected assuming ~30% was root respiration and ~70% from organic matter decomposition). The turnover times they calculate ranged from 10 years in tropical grasslands to ~500 years for tundra and wetland environments, with a global average of 32 years.

Case 1. Bulk radiocarbon age is 2770 years. Homogeneous pool at steady state



Case 2. Same bulk age, but two components with different turnover times



**Figure 5.** Illustration of how age and turnover time may be confused using radiocarbon data. Case 1 is a single, homogeneous reservoir, with a  $^{14}$ C content equivalent to a turnover time of 2,770 years (0.78 fraction Modern; see Appendix 1). If there are ten kilograms of carbon in the reservoir, the annual flux in or out of the reservoir at steady state, Flux = 10,000 g/2,770 y = 4 g C/y. In Case 2, the soil organic matter is assumed to be a two component mixture, with two thirds of the carbon having a turnover time of 20 years, and one third with a turnover time of 10,000 years. The overall  $^{14}$ C content is the same as in Case 1, but the annual flux is now Flux = (6,670 g/20 y) + (3330 g/10,000 y) = 330 g/y. So the bulk turnover time may tell you little about the details of how fast the system will respond to changes in inputs or decomposition rates associated with land use or climate change.

The radiocarbon content of SOM provides a measure of the average age of C atoms. Radiocarbon measurements of SOM made in the early 1960s, or on archived soils collected and stored since that period, showed the average age of soil C to be several hundreds to thousands of years in

temperate and some tropical systems. The apparent contradiction with Raich and Schlesinger's results may be explained if most of the flux of CO<sub>2</sub> from the soil is derived from decomposition of "young" carbon, whereas much of the C residing in the soil is stabilized and decomposing only very slowly. In other words, instead of a large C reservoir with 10-year turnover in tropical grasslands, there is likely a small reservoir of annual-cycling organic matter and a much larger one with cycling on time scales of several decades to a century. The distinction is important if we want to predict the response rate and magnitude of the grassland soil to disturbances like management or climate change.

One key area of work in understanding and modeling soil C is the study of relative decomposition rates for various organic substrates and organic matter byproducts. While the compounds comprising organic matter form a continuum of decomposability, a continuous distribution of turnover times is difficult to constrain using field measurements. There is general agreement that the distribution of SOM decomposition rates tend to cluster at three very different time scales. Root exudates and components of fresh plant litter decompose on the time scales of hours to months and are referred to as the "active pool." Stabilized organic matter persists in soils over several thousands of years and is often referred to as the "passive" or "millennial cycling" C pool. The remaining "intermediate" or "slow" C has turnover times in the range of years to centuries, and may consist of structural components of plants more resistant to decay, or organic compounds that have been weakly stabilized by their association with mineral or aggregate surfaces. We will divide our discussion of C dynamics by the time scale involved in decomposition.

### Observational Constraints for Determining C Dynamics in Soils

No single satisfactory method yet exists by which to separate soil C into components with different turnover times. Instead, the dynamic makeup of soil C is deduced using many constraints, including: physical and chemical fractionation of organic matter, field and laboratory decomposition studies, measures of C fluxes into and out of the soil, measurements of <sup>14</sup>C in soils sampled at various times before and after the peak of atmospheric nuclear weapons testing, changes in the <sup>13</sup>C content of SOM following a vegetation change from plants with C<sub>3</sub> to C<sub>4</sub> photosynthetic pathways, and measurements of changes in the total amount of C in soils of different age or following disturbance. Each of these tools is suitable for determining different time scales of soil C dynamics.

#### Litter Decomposition Experiments

The rate of mass loss of fresh plant litter may be used to estimate decomposition rates, assuming first order kinetics:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -kM; \ k = -t^{-1} \ln \left( \frac{M_t}{M_0} \right)$$

where  $M_0$  is the initial mass and  $M_t$  is the mass at time t after deployment. This method is complicated by the design of the containment system for the plant litter, which needs to allow soil fauna in but not mass transport out. Most field litter-bag experiments show relatively rapid

initial rates of loss, followed by slower decomposition of the remaining recalcitrant compounds. Decomposition rates vary with climate (fastest decomposition in hot, moist climates, and slowest in cold, wet climates), the type of plant material (roots versus leaves, lignin versus cellulose), soil fauna, and soil texture. Isotopically labeled C (enriched in <sup>13</sup>C or <sup>14</sup>C) may be added to soils (either as labeled plant material or as individual organic compounds) to follow specific decomposition pathways. These studies have shown that, while much of the labeled material may decompose rapidly, a portion is incorporated into components that are more stable and remains in the soil for many years.

## Laboratory Incubations

Laboratory incubations provide a controlled environment where the effect of variables like temperature on decomposition rates may be studied independent of confounding factors often found in field experiments. A known quantity of soil is sealed in a jar, and the amount of CO<sub>2</sub> evolved is monitored over time. Most incubations are conducted under conditions far removed from those found in the field—for example, temperatures may be elevated so as to "burn off" C more rapidly. Microbial populations may adjust during the experiment until they do not resemble *in situ* populations. Hence, while incubations may give reliable information about how decomposition rates might respond to changes in temperature and moisture, they are unlikely to be reliable representations of decomposition rates in the field.

#### Soil Respiration

Soil respiration, of the efflux of CO<sub>2</sub> from soils to the atmosphere, is one of the fundamental flows in the terrestrial carbon cycle. It is the primary way that carbon moves from ecosystems back to the atmosphere. Globally, soil respiration is one of the largest fluxes, an estimated 50–80 Pg C/y (Potter et al., 1993; Raich and Schlesinger, 1992; Schimel, 1995). Since the annual exchange of C between the soil and atmosphere is so large (by comparison, we add only ~6 Pg C/year to the atmosphere by fossil fuel burning), interannual variability in soil respiration may potentially cause changes in the rate of increase in atmospheric CO<sub>2</sub> (Trumbore et al., 1995). Soil respiration makes up >50% of total ecosystem respiration (which in turn roughly equals gross photosynthesis in ecosystems). Soil respiration thus varies with latitude, from 80 g C m<sup>-2</sup> y<sup>-1</sup> in deserts to 800–2000 g Cm<sup>-2</sup> y<sup>-1</sup> in a tropical forests (Raich and Potter, 1995; Raich and Schlesinger, 1992; Schlesinger, 1977; Trumbore et al., 1995).

Soil respiration has two sources: (1) decomposition of SOM by microbes (heterotrophic respiration) and (2) respiration from live plant roots (autotrophic respiration). It is difficult to directly determine the amount of respiration from each of these sources separately, and thus to track decomposition rates *in situ*. As a result, it has proven very difficult to observe the effect of soil temperature, moisture, and other factors on decomposition directly in the field. Potential changes in CO<sub>2</sub>, temperature, and moisture regimes in the coming decades will likely influence autotrophic and heterotrophic respiration in different ways. For example, a commonly cited response of plants to elevated CO<sub>2</sub> is increased allocation to roots. However, to see this response in the field, one must prove that root activity is increasing and not decomposition rates.

The most common method of measuring soil respiration is to place a chamber over the soil and measure the change in CO<sub>2</sub> concentration in the headspace over time. For a continuous 24-hour measurement, the CO<sub>2</sub> is trapped in soda lime in the chamber. This soda lime method may be

useful for determining relative soil respiration rates and for integrating over a diurnal cycle. The long incubation time for the soda lime method leads to large chamber effects that likely create substantial artifacts in the flux measurements. For more rapid and more accurate measurements, changes in the CO<sub>2</sub> concentration in the chamber headspace are monitored over time, using either syringe samples analyzed with a gas chromatograph or by circulating chamber air through an infra-red gas analyzer. Eddy covariance methods (discussed in Valentini, NATO ASI) can measure gross photosynthesis and respiration by the whole ecosystem, but, except where a below-canopy eddy flux system is employed, do not separate soil respiration from aboveground respiration without using a model to predict aboveground respiration.

### Isotopic Tools

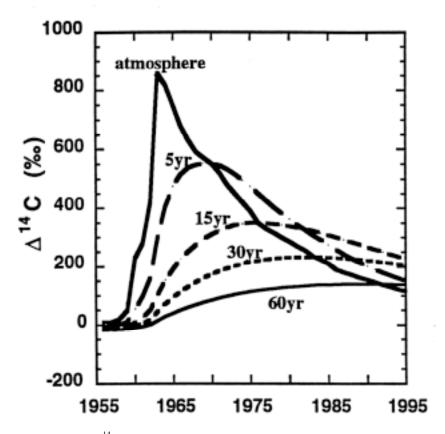
Carbon has three isotopes: 98.89% of earth's C is  $^{12}$ C,  $\sim 1\%$  is  $^{13}$ C (a stable isotope) and  $\sim 10^{-10}\%$  is  $^{14}$ C (radiocarbon, a radioactive isotope). Both rare isotopes have proved useful in deciphering soil C dynamics.

### Stable C Isotopes

For the special case where a vegetation change from C<sub>3</sub> to C<sub>4</sub> plants (or *vice versa*) has occurred, the rate of change of C isotopes in SOM will give an idea of the turnover time of SOM. Veldkamp (NATO ASI) discusses this method, which has been used frequently in tropical pastures planted with C<sub>4</sub> grasses that have replaced C<sub>3</sub>-dominated forest. There are two drawbacks to this method: (1) it cannot be used to study soils that have not undergone a vegetation change; and (2) it requires careful measurement of C inventory changes in disturbed versus undisturbed soils. These attempts are complicated by plowing, disking, and/or erosion of the pasture soils, as well as the inherent uncertainty in bulk density determinations.

### Radiocarbon

Radiocarbon (<sup>14</sup>C) is unstable, and decays by emission of an electron to form <sup>14</sup>N, with a half-life of 5,730 years. It is continuously produced in the upper atmosphere by interactions of highenergy cosmic rays with the upper atmosphere. The <sup>14</sup>C is oxidized to <sup>14</sup>CO<sub>2</sub> within a few weeks, and mixed into the troposphere (the lower, well-mixed part of the atmosphere), where it is taken up by plants during photosynthesis and may dissolve in the surface waters of the ocean. If a C reservoir ceases to exchange <sup>14</sup>C with the atmosphere, the <sup>14</sup>C it contains will begin to decrease because of radioactive decay. This is useful for studying very stable C pools in soils, since they reside long enough for significant decay of <sup>14</sup>C to occur. The longest time scales that can be addressed with <sup>14</sup>C in this way are on the order of 60,000 years.tmospheric thermonuclear weapons testing, which peaked in 1963, approximately doubled the amount of <sup>14</sup>C in the atmosphere (Figure 6). This "bomb" <sup>14</sup>C provides a global isotopic tracer for the C cycle. The degree to which bomb <sup>14</sup>C is found in SOM provides a direct measure of the amount of fastcycling (active+slow) SOM. The most straightforward approach compares <sup>14</sup>C measurements of SOM sampled prior to 1960 with contemporary samples from the same location. Where no archived soils are available, however, radiocarbon measurements must be combined with other observational constraints to separate the radiocarbon signature of rapidly cycling from very refractory organic matter. The time scales of C turnover that may be addressed using bomb <sup>14</sup>C range from  $\sim$ 2 to  $\sim$ 100 years.



**Figure 6.** Change in atmospheric  $^{14}$ C with time in the northern hemisphere (heavy solid line) since 1955. Radiocarbon values are expressed as the per mil variation in  $^{14}$ C/ $^{12}$ C ratio relative to a standard (see Appendix for definition of units). The other lines show the evolution of  $^{14}$ C for homogeneous, steady-state reservoirs with turnover times of 5, 15, 30, and 60 years.

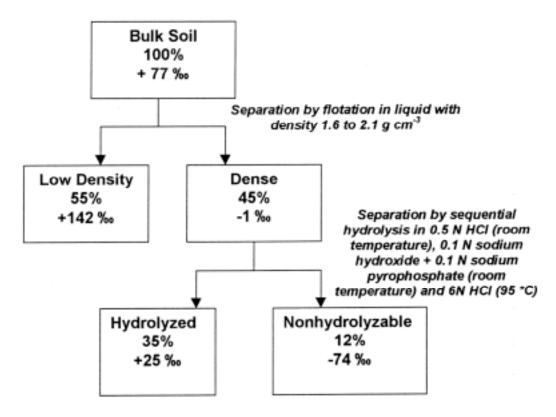
Direct measurement of the age of C atoms leaving the soil is possible by trapping air from the headspace of a chamber (Dörr and Münnich, 1986). The degree to which <sup>14</sup>C reflects recently fixed C versus C fixed several years to decades ago provides a potentially important tool for partitioning the sources of soil respiration (autotrophic plant respiration versus heterotrophic microbial respiration) and the turnover times of the decomposing organic matter that contributes the most to soil respiration. Dörr and Münnich (1986) found significant seasonal differences in the <sup>14</sup>C content of soil respiration, with summer emissions dominated by recently fixed carbon, and winter fluxes by carbon fixed up to several decades previously.

Appendix 1 contains a more thorough discussion of radiocarbon methods and applications to SOM studies.

### Fractionation of Soil Organic Matter

A variety of approaches have been used to separate organic matter physically and chemically into more labile and more recalcitrant components. Most of the components are "operationally defined," meaning that the properties of the organic matter fractions are defined primarily by

what was done to isolate them. Two methods have been used in conjunction with radiocarbon measurements that appear to separate organic matter into components for which the average age of C are vastly different (Figure 7). The first of these involves a density separation (Spycher et al., 1983), where the organic matter that floats in a solution of density 1.6–2.0 g/mL is made up of relatively undecomposed plant material, charcoal, and pollen. The organic matter that sinks in the heavy liquid is associated with soil minerals (which have density >1.6 to 2.1 g/ml). Carbon contents and C/N ratios of low-density material are high (generally 10–40%C) compared to the organic matter in the material with density >1.6-2.1 g/mL (<10%C). Radiocarbon measurements (see Appendix 1) confirm that low-density organic matter has younger average ages than organic matter in the dense fraction. Low-density carbon is approximated by the carbon trapped on a coarse (>63 micron) sieve (Cambardella and Elliott, 1994; Trumbore and Zheng, 1997). Different methods of preparing the soil sample (sieving, disaggregation, picking for roots) influence the yield of C in the low-density fraction—indicating that pre-treatment may influence the results of many measures of soil C.



**Figure 7.** Fractionation scheme for separating soil organic matter. In each box are listed the soil fraction, the percent of bulk soil carbon that was found in that fraction, and the  $\Delta^{14}$ C in parts per mil (‰) for that fraction. Data are from the 20–40 cm depth interval of soils in a dry coniferous forest in the Sierra Nevada mountains of California (Trumbore and Zheng, 1997). The data show that the low-density C has the fastest, and the non-hydrolyzable residue the slowest, turnover times. Size separation with this soil did not separate C into components with different turnover times.

A second method for fractionation of organic matter separates those components soluble in acid or base from insoluble compounds. As fresh plant matter contains both soluble and insoluble components of the same age (Ertel and Hedges, 1984), hydrolysis is best performed following a

density separation. Studies with radiocarbon have shown repeatedly that the non-hydrolyzable residue has older average ages than does the material that is solubilized in acid and base (Trumbore and Zheng, 1997). The term "humic compounds" refers specifically to those extracted in base, while the residue is referred to in the literature as humin. Problems with the hydrolysis procedures include condensation reactions that may lead to the formation of refractory compounds from molecules originally in solution.

Several other methods for fractionating organic matter exist, including separation of soil components by size and degree of aggregation (using incubations), and by combustion under increasingly severe conditions. As yet, no one fractionation method has been found that works all the time for all soils.

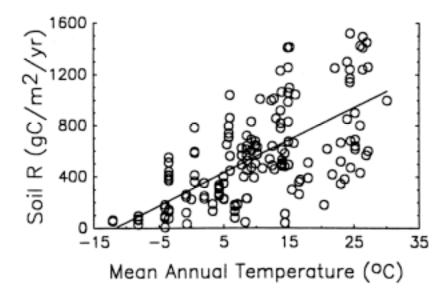
#### IMPORTANT CONTROLS ON C DYNAMICS

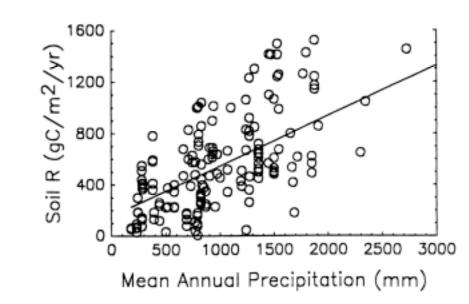
Application of the methods described above to the study of organic matter has led to several generalizations about the controls of carbon turnover in soils. These generalizations of climate and vegetation controls are built into most ecosystem models. The models split SOM into several pools with different turnover times. Each pool is assigned a maximum decomposition rate, which is set by the characteristics of the plant material and then modified by factors associated with soil temperature, moisture, and texture. Estimates of the global partitioning of SOM into faster-cycling and stabilized portions are extremely uncertain. To date, the only concerted effort at partitioning SOM globally has been done using the CENTURY and CASA ecosystem models (Parton et al., 1987; Potter et al., 1993; Raich and Potter, 1995; Schimel et al., 1994), which extends only to 20 cm depth.

### Time Scales of Months to Centuries—"Active" C Pools

Climate exerts the dominant control over decomposition rates and the turnover of SOM. Laboratory incubations have been used to show the sensitivity of decomposition rates to soil temperature and moisture conditions. In general, the amount of  $CO_2$  produced per gram of organic C in soil increases with increasing temperature. At temperatures above freezing, this rate of increase is approximately exponential and is expressed as  $Q_{10}$  values (where the  $Q_{10}$  is defined as the rate at a temperature  $10^{\circ}$ C higher than a reference temperature, divided by the rate at the reference temperature). Lloyd and Taylor (1994) argue against the concept of the  $Q_{10}$ , since the response of respiration to temperature is not the same across all temperature ranges. For example, based on laboratory incubations, Kirschbaum (1995) argues that  $Q_{10}$  values increase with decreasing soil temperature (that is, the increase in respiration rates is greater between -5 and +5°C than between 5 and 15°C).

Field soil respiration measurements also show a strong link between climate and CO<sub>2</sub> fluxes at the global scale (e.g., Figure 8), though the temperature-respiration response relationship at any given site may differ from the global relationship. Davidson et al. (1997) summarize several of the controls of soil respiration that may be confounded with temperature, including moisture, and changes in the seasonal activity of autotrophs and heterotrophs.

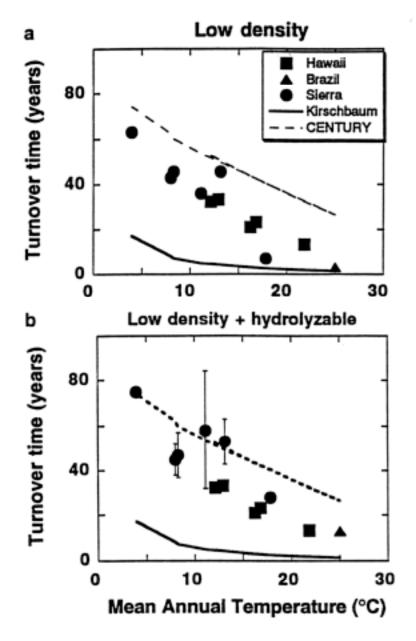




**Figure 8.** (A) Soil respiration and mean annual air temperature for a number of sites worldwide. (B) Soil respiration and mean annual precipitation. Net primary production is also correlated with soil respiration at the same sites. Source: Raich and Schlesinger, 1992.

Estimates of the turnover time of SOM, determined using C isotopes combined with other information, also show the temperature dependence of decomposition rates (e.g., Townsend et al., 1995; Trumbore et al., 1996). Figure 9 compares the turnover rates derived from <sup>14</sup>C for low density and hydrolyzable SOM from climosequences located on elevation gradients with results from Kirschbaum's literature summary of incubation data. The two curves differ in part because the pools studied by short-term incubation are smaller and turn over more rapidly than those studied using bomb radiocarbon. However, the strong dependence of turnover on temperature for several kinds of soils and ecosystems is clear. Trumbore et al. (1995) used the temperature

relationship in Figure 9, together with estimates of the amount of C in fast-cycling organic matter pools, to show that interannual variations of  $CO_2$  emitted by decomposition due to temperature variations are potentially large enough to significantly affect atmospheric  $CO_2$ .



**Figure 9.** Comparison of turnover rates from <sup>14</sup>C (points) analyses along elevation gradients in the Sierra Nevada and Hawaii, with model-derived estimates of turnover from the CENTURY model (Schimel et al., 1994) and the summary of incubations by Kirschbaum (1995). Turnover times from radiocarbon are presented for two fractions of SOM: low-density C, and low-density C plus that which is hydrolyzed by acids and bases (see Figure 7). Source: Trumbore, 1997.

Responses to soil moisture show that rates of CO<sub>2</sub> evolution are inhibited by both very low and very high moisture contents. Under dry conditions, lack of water limits microbial activity. Under humid or wet conditions, moisture becomes limiting to oxygen diffusion and thus to aerobic

mineralization of C. Soil respiration measurements across drainage gradients at the same site show lower fluxes at more poorly drained sites, as well as a reduction in fluxes at well-drained sites during drought conditions (Davidson et al., 1997). However, it is not clear to what degree changes in ecosystem productivity versus decomposition rates are responsible for differences in CO<sub>2</sub> emissions. Partitioning of soil respiration into autotrophic and heterotrophic components would help in this regard.

Vegetation, which is also related to climate, is another important control of C turnover. Plant functional groups differ widely in the decomposability of their litter and roots. For example, the leaves shed each autumn by broadleaf deciduous trees break down more rapidly than the needles of conifers. Within a plant species, the decomposability of litter can vary with the nutrient and water status of the plant, and response to herbivory. Effects of climate and vegetation become hard to separate in the field. For example, conifers are found in colder and wetter (or drier) climates than deciduous forests—it is hard to say whether decomposition rates in coniferous forests are slower because of climate or the inherent decomposability of the litter.

### Millennial and Longer Time Scales

The controls over the stabilization and storage of SOM with very long turnover times ("passive" or "millennial cycling" C pools) are less well understood than those for fast-cycling carbon. Climate appears to be the dominant control only at climatic extremes: In wetland or saturated soils, oxygen depletion strongly inhibits decomposition to CO<sub>2</sub>, leaving the slower anaerobic process of methane formation. In extremely cold environments, the biologically active season may be very short. These conditions lead to long-term storage of organic material in soil. It appears that organic matter that is "climatically stabilized" in this way may be readily decomposed if the soil becomes warmer or drier, as a result, for example, of draining peat bogs or climatic warming.

In most of the world's soils (i.e., in moderate climates), there are two main mechanisms of long-term carbon stabilization: (1) the physical and chemical protection afforded by soil minerals and soil aggregates and (2) biological production of recalcitrant compounds, either through humification or as cell by-products. Soil minerals and soil aggregates physically protect organic material in interstitial spaces that are too small for microbial decomposers to penetrate (Oades, 1988). Minerals also form chemical protection by forming stable bonds with the organic material, leaving it energetically unavailable. These bonds may take the shape of a thin coating of organic matter formed around clays (Mayer, 1994), or chelates with, for example, aluminum or iron (Boudot, 1992). Carbon stabilization by noncrystalline minerals also slows decomposition of labile substrates (Saggar, 1994) in surface soils.

#### POTENTIAL SOM FEEDBACKS TO GLOBAL ENVIRONMENTAL CHANGE

Global patterns of carbon storage in soils reflect the balance of plant productivity and decomposition, the major controls of carbon inputs to and losses from soil. The likely causes of future changes in soil C cycling are changes in vegetation composition and productivity, land management, and climate.

### **Changes in Ecosystem Production**

Plant productivity is determined by many factors, including climate, soil fertility, and plant species composition. In general, warmer, wetter environments have the highest net primary productivity (NPP). Some global environmental changes, such as increased atmospheric CO<sub>2</sub> and N deposition, are likely to cause an increase in plant productivity, at least in the short term. Other atmospheric pollution, namely increased tropospheric ozone, acid rain, and stratospheric ozone depletion, are predicted to decrease NPP. Although increased temperatures by themselves lead to increased rates of photosynthesis in many ecosystems, it is not yet clear what the response of global NPP will be to the suite of climatic changes accompanying global warming.

If plant productivity increases without an increase in decomposition rates, more carbon will be sequestered in soil. Since decomposition is proportional to the stock of SOM, SOM will build up until the efflux from decomposition reaches a level roughly equal to the higher rate of inputs. Fast-cycling pools will adjust most rapidly to new steady state conditions. Assuming a CO<sub>2</sub> fertilization response of 0.35 times NPP and turnover time of fast-cycling C of 25 years, Harrison et al. (1993) calculated that increased C inputs to soils from CO<sub>2</sub> fertilization should have resulted in net storage of 0.5 Pg C/y in fast-cycling C and 0.1 Pg C/y in surface litter in the 1980s. This study, however, assumed no change in decomposition rates in response to the increased carbon stocks. In the long term, it is unlikely that plant productivity could continue to increase with increasing atmospheric CO<sub>2</sub>, due to widespread limitation of NPP by water or nutrients, or because of acclimation of plants to higher CO<sub>2</sub> conditions. The turnover time of 25 years determined by Harrison et al. is for bulk organic matter; if this in turn consists of components that cycle more rapidly and more slowly than 25 years, their predicted response is likely an underestimate for the short term and an overestimate for the long term.

After CO<sub>2</sub> fertilization, the most often-cited mechanism leading to a terrestrial carbon sink is enhanced nitrogen availability to plants due to enhanced nitrate deposition (Melillo et al., 1995; Schimel, 1995). Nitrogen availability will also increase, at least in the short term, if there is net decomposition of SOM, since soil organic matter is a major source of N for plants. The degree to which this mechanism can operate depends on the "leakiness" of the ecosystem with respect to nitrogen—in other words, how much of the available N is actually associated with enhanced plant growth. For more discussion, see Houghton et al. (1998).

Changes in global or regional C inventory on the order of 1 Pg of C are impossible to measure directly (Post et al., 1995; Trumbore et al., 1995) in soils. For example, a 0.5 Pg C/y sink integrated over 30 years increases the global soil C pool only 1%. C inventory measurements, plagued by small-scale heterogeneity and comparatively large analytical uncertainties, are generally restricted to observing inventory changes on the order of 10–20%.

### **Climate Changes**

Both vegetation inputs and decomposition rates are expected to increase with increases in temperature (all other factors remaining equal). Soils become an amplifying feedback if the

temperature dependence of decomposition is steeper than that of plant productivity. Schimel et al. (1994) summarize modeling and databased predictions of C release from SOM for a 1°C increase in global mean annual temperature. The calculated net release ranges from 11.1 to 33.8 Pg C once a new steady state is reached. The smallest release is predicted by CENTURY, which accounts for feedbacks between plant productivity and release of nutrients that accompanies net SOM decomposition. In N-limited plant communities, the release of N through increased decomposition in a warmer world could further stimulate plant growth, and even cause net sequestering of C as nutrients are transferred from soils (low C/N rations) to plant reservoirs with higher C/N ratios.

The timing of the decomposition responses to increased temperature depends on the partitioning of C among fast- and slow-cycling pools. Results of modeling and radiocarbon studies show that up to a third of the C stored in the top one meter of soils is in fast-cycling forms. The fastest and strongest response will come from areas with large fluxes and rapid turnover rates. Hence, Townsend et al. (1995) and Trumbore et al. (1996) predict that tropical regions will dominate short-term, interannual, response to climate variations.

The large stores of C in northern wetlands (which contain an estimated one-fifth of the total global soil C reservoir) are mostly climatically stabilized. If warmed and dried, it is clear that climatically stabilized organic matter is capable of decomposing rapidly, leading to a large positive feedback to CO<sub>2</sub>-induced climate change. Indeed, year to year differences in decomposition of old stores of humic materials in some boreal forest soils may determine the status of the entire stand as a net source or sink of C (Goulden et al., 1998). Because overall fluxes at boreal and higher latitudes are small compared to those in the tropics, it is unlikely that even large interannual variability in C storage may be as important in affecting the very short term (years and shorter) C balance of the atmosphere. However, the potential for a longer-term (years-to-decades), large response of soil C to climate change is greatest at higher latitudes, because more C is stored there in potentially decomposable forms.

One consequence of all studies of C turnover as a function of temperature is that soils should presently be a net source of C to the atmosphere, because of documented temperature increases over the past century.

### Land Cover or Land Management Change—Disturbance

Disturbances that affect C cycling include fires and floods, and deforestation, reforestation, agriculture, and drainage of fields/bogs/forests/wetlands. Disturbance affects C inputs and losses to soil by changing vegetation, soil structure, temperature, water balance, and nutrient availability. Rates of change in organic C stocks in response to disturbance can be an order of magnitude larger than those associated with response to increased productivity or climate variability, because the changes in ecosystem inputs and decomposition rates are more extreme for disturbance than those predicted for climate changes.

Rapid rates of C accumulation and loss may occur over shorter time scales as the large component of fast-cycling soil C responds to disturbance (such as a change in vegetation). Soils may lose a significant portion of their carbon following cultivation if native ecosystems are

replaced by less productive ones; these changes represent a loss of fast-cycling C rather than passive C pools (Davidson and Ackerman, 1993; Harrison and Broecker, 1993; Stallard, 1998; Trumbore et al., 1995). In some cases, increased productivity has increased C stocks in soils (e.g., Trumbore et al., 1995; Veldkamp, NATO ASI volume). Hence, soil carbon is a resource that is potentially manageable, particularly in agricultural lands.

Chronosequence studies show most rapid C accumulation in young soil surfaces. Stallard (1998) hypothesizes that large-scale erosion may have resulted in an enhanced C sink in continental interiors. Assuming the eroded C is not decomposed where it is deposited (or decomposes more slowly than it would have had it remained *in situ*), the rapid accumulation in the exposed, eroded surfaces would be a net sink of atmospheric CO<sub>2</sub>.

Work in fire-dominated ecosystems such as boreal forests and Mediterranean chaparral shows high rates of net C sequestration in regrowing vegetation and surface detritus in the decades in between fire events. In these systems, decomposition is slow enough to be less important than periodic fire for returning CO<sub>2</sub> to the atmosphere. Thus, changes in fire frequency linked to climate or to land use (for example, fire suppression) may ultimately control a region's status as a C source or sink. When planning deployment sites for eddy covariance measurements of Net Ecosystem Production (NEP), it is wise to consider how the disturbance response status will influence the measured NEP at the site.

#### Are Soils Net Sources or Sinks of Carbon?

As soils and ecosystems develop, they gain and lose C. For example, approximately 25% of the world's SOM is stored in soils that began developing after the last major deglaciation (Harden et al., 1992). Based on chronosequence studies, these soils are now functioning as long-term sinks for atmospheric CO<sub>2</sub>. Similarly, we predict that older soils may be acting as long-term net sources of CO<sub>2</sub> to the atmosphere because of declines in NPP and in weathering of minerals to more stable forms. In the pre-1850 world, it is unclear whether soils could have been assumed to be at steady state. However, net fluxes between soils and the atmosphere have been accelerated by large-scale land-cover changes over the past century.

On decadal to century time scales, the net C balance of soils may be dominated by disturbance regime and frequency. At the stand level, ecosystems recover from events such as large storms (blow-downs), fire, insect mortality, or floods. Disturbance-dominated regimes are characterized by short periods of rapid C loss (e.g., through burning in fires), followed by longer periods of C sequestration. Net C accumulation between disturbances may be rapid compared to the long-term rates associated with the formation and loss of soil minerals. However, when averaged over long times or large spatial scales (many stages of disturbance), the long-term rates should dominate.

Superimposed on the decadal to century timescales associated with disturbance and recovery are the interannual changes in C storage in soils. The lag time between C uptake by photosynthesis and respiration, together with the amount of C uptake and loss, will determine the magnitude of interannual variability. For example, if most organic C is respired within a year of when it is fixed by plants, enhanced plant productivity in a given year will be offset by increased decomposition in the same year. However, if lag times are significantly longer than 1 year on average, higher than

average productivity in one year would lead to net C sequestration, with net C loss in following years, as the pulse of high productivity is decomposed slowly over time. These effects are expected to be largest in regions where C fluxes are greatest into plants and out of soils, and where a significant time lag exists.

### **SUMMARY**

SOM is an important source and sink of atmospheric  $CO_2$  on several time scales. Enough C is stored in organic forms that exchange rapidly with atmospheric  $CO_2$  for soils to be important components of the global C cycle during the coming century. The major controls on C turnover, temperature, moisture, and vegetation are likely to change in the coming decades. Our ability to predict the response of the soil C reservoir either locally or globally is still limited.

#### APPENDIX 1. MORE ON RADIOCARBON AND ITS USE IN SOILS

## Methods of Radiocarbon Analysis and Reporting of <sup>14</sup>C Data

### **Sample Preparation**

There are two methods for measuring radiocarbon: decay counting and accelerator mass spectrometry (AMS). Decay counting measures the electrons emitted during radioactive decay of <sup>14</sup>C back to <sup>14</sup>N. Because the half-life of <sup>14</sup>C is 5,730 years, relatively large samples (several grams of carbon) are required to obtain enough decays for a measurement comfortably above background levels. AMS directly measures the ratio of <sup>14</sup>C to <sup>13</sup>C and <sup>12</sup>C atoms in the sample, using a high-energy accelerator as an inlet to a mass spectrometer. The sample size needed is much smaller, on the order of 1 mg of carbon.

Organic matter must first be completely combusted to  $CO_2$  for all <sup>14</sup>C measurements in soils. For small samples (AMS), this is accomplished by sealing enough homogenized sample to make ~1 mg of C with cupric oxide wire and a small piece of silver wire in an evacuated quartz tube (Buchanan and Corcoran, 1959). The  $CO_2$  produced is purified cryogenically and then reduced to graphite using a zinc- or iron-catalyzed reduction method described in Vogel (1984). The graphite target is used for AMS. Larger samples (for decay counting) are combusted at similar temperatures in a large vacuum line (Goh, 1991). The resulting  $CO_2$  is cryogenically purified, then counted directly (for some decay counting lines) or converted to acetylene or benzene (for other decay counting). For more details on experimental methods, see Goh (1991) and Trumbore (1996).

## Reporting of <sup>14</sup>C Data

The amount of  $^{14}$ C in a sample is reported as a ratio to a known standard. Specifically, the fraction Modern of a sample is its ratio to 0.95 times the activity of an oxalic acid standard prepared by the U.S. National Bureau of Standards (NBS, now called the U.S. National Institute of Standards and Technology, NIST) measured in 1950, corrected to  $\delta^{13}$ C of -19‰). This ratio is the fraction Modern (Modern is by definition 1950):

$$F = \frac{\left(\frac{14C}{12C}\right)_{sample(-25)}}{\left(\frac{14C}{12C}\right)_{ox1(-19)}}$$
(A1)

where the sample has been normalized to a  $\delta^{13}$ C of -25% to account for isotopic fractionation effects (Stuiver and Polach, 1977). The  $^{13}$ C correction is important. For example, the  $\delta^{13}$ C difference between atmospheric CO<sub>2</sub> and carbon fixed during photosynthesis by C<sub>3</sub> plants is approximately 20%. Assuming the fractionation of  $^{14}$ C will be roughly twice that of  $^{13}$ C (since the mass difference between 12 and 14 is twice that between 12 and 13), the  $^{14}$ C content of a tree

and the  $CO_2$  which it is fixing through photosynthesis will differ by approximately 40‰, even though both  $CO_2$  and the tree are the same "age." To account for fractionation effects, all samples (with  $\delta^{13}C$  of  $\delta$ ) are corrected to a constant  $^{13}C$  content (-25‰):

$$F_{-25} = F_{\delta} \frac{1 - 25/1000}{1 + \delta/1000}$$
 (A2)

The conventional radiocarbon age is then:

$$^{14}C \text{ age} = -t \ln F \tag{A3}$$

where t is the Libby mean life of radiocarbon, 8,033 years.

Geochemists commonly use a different way of reporting <sup>14</sup>C data: the deviation in parts per thousand (per mil) from the absolute standard:

$$\Delta^{14}C = 1000 \times \left[ F \times \exp^{\left(\frac{-(y-1950)}{8267}\right)} - 1 \right]$$
 (A4)

where the exponential term is used to correct the oxalic acid standard measured in year y to its absolute (1950) value. The exponential term in Equation (4) takes into account the radioactive decay of the standard, since the absolute isotope ratio of the standard measured in 1950 will be greater than it will be in subsequent years.

Using the geochemical notation, positive values of  $\Delta^{14}$ C indicate the presence of bomb-produced  $^{14}$ C, and negative values indicate the predominance of C fixed from the atmosphere long enough ago for significant radioactive decay of  $^{14}$ C (half-life = 5,730 years) to have occurred. The analytical precision for determination of  $^{14}$ C for graphite targets averages  $\pm$  4–8‰ for samples containing bomb  $^{14}$ C (depending on the methods used for sample preparation and measurement).

### Modeling C Dynamics Using Radiocarbon Measurements

#### Steady-State Systems

Natural Radiocarbon

SOM is a heterogeneous reservoir with a variety of turnover times, to which carbon is continuously added (as new plant matter) and lost (as leached organic carbon or  $CO_2$ ). The radiocarbon content of SOM cannot be interpreted as a "date," but represents the average age of a carbon atom in the soil reservoir. For a homogeneous carbon-containing reservoir, i, with input rate  $I_i$ , first-order decomposition constant  $k_i$ , and carbon content  $C_i$ , the balance of carbon is:

$$\frac{dC_i}{dt} = I_i - k_i C_i \tag{A5}$$

For a steady-state reservoir,  $k_i = I_i/C_i$ . The turnover time (t) is defined as  $1/k_i$  (at steady state, this equals the inventory of carbon divided by the input rate). The balance of  $^{14}C$  atoms in the

same reservoir ( $^{14}C_i = f_iC_i$ , where  $f_i$  is the fraction Modern) will reflect the rate of decomposition,  $k_i$ , and the rate constant for radioactive decay of  $^{14}C$ ,  $\lambda$  ( $\lambda = 1.210 \times 10^{-4} \text{ y}^{-1}$ ):

$$\frac{\mathrm{d}f_{i}}{\mathrm{d}t} = \left(\frac{1}{C_{i}}\right) \left(I_{i} f_{atmosphere} - (k_{i} + \lambda) f_{i} C_{i}\right) \tag{A6}$$

At steady state,

$$f_i = \binom{1}{C_i} (I_i / (k_i + \lambda)) \tag{A7}$$

Since at steady state,  $C_i = I_i/k_i$ , Equation (7) may be rewritten as:

$$f_i = (k_i/(k_i + \lambda)) \tag{A8}$$

For components with short turnover times  $(k_i >> \lambda)$ , a calculated  $^{14}C$  age will approximate the turnover time,  $\tau$   $(1/k_i)$ . For components with  $k_i$  equal to or less than the decay constant for radiocarbon, the age will be less than the turnover time. For example, the  $^{14}C$  age calculated for a steady-state reservoir with  $k_i = 0.01$  y<sup>-1</sup> ( $\tau = 100$  years) would be 100 years, while that for a component with  $k_i = 0.0002$  y<sup>-1</sup> ( $\tau = 5000$  years) would be 3,910 years.

#### Bomb Radiocarbon

For a steady state system, a time-dependent model is used because of the irregular shape of the atmospheric <sup>14</sup>CO<sub>2</sub> record.

$$F_C(t) = \frac{\left[I * f_{atm}(t) - C(t-1) * F_C(t-1) * (1-k-\lambda_{14})\right]}{C(t)}$$
(A9)

Since the reservoir is at steady state, C(t-1) = C(t) = I/k, Equation (9) reduces to:

$$F_C(t) = kF_{atm}(t) + F_C(t-1)(1-k-\lambda_{1.4})$$
(A10)

Figure 6 in the text shows the 1996 predicted values of  $^{14}$ C for a homogeneous, steady state reservoir with different turnover times. For turnover times <50 years, it is clear that two different turnover times may yield the same  $\Delta^{14}$ C value. To distinguish which of these two turnover times is correct, we use one of two methods. First, if an archived sample from the same soil is available, radiocarbon measurements may distinguish between the two possibilities. Organic matter with shorter turnover times will have decreased  $^{14}$ C over the past several decades, while those with longer turnover times will have increased in  $^{14}$ C. If no archived soil is available, knowledge of the C fluxes into and out of the soil may be used to determine the correct turnover time.

The  $\Delta^{14}$ C values measured in low-density organic matter isolated from the A horizon of a soil sampled in 1956 and 1992 in the Sierra Nevada mountains were -31 ‰ and +127 ‰, respectively (Trumbore et al., 1995). This  $^{14}$ C increase is consistent with either a turnover time of 5 or 57 years. The total amount of low-density carbon in the A horizon was 6.5 kg C m<sup>-2</sup>, with low-density carbon accounting for nearly 90% of the carbon in this layer. The 5-year turnover time

implies annual C inputs from litter of  $\sim 1,300~g$  C m<sup>-2</sup> yr<sup>-1</sup>, while the 57-year turnover time implies inputs of only 114 g C m<sup>-2</sup> yr<sup>-1</sup>. The measured aboveground litterfall at a nearby site was  $\sim 100~g$  C m<sup>-2</sup> yr<sup>-1</sup>. Hence, the most reasonable turnover time is 57 years for the low-density organic matter in the A horizon.

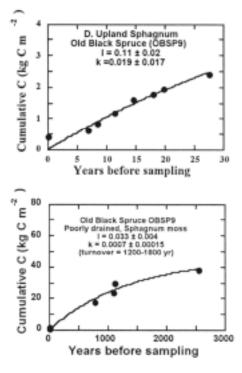
A potential problem with this approach is the uncertainty as to whether the reservoir under consideration is homogeneous. Bulk SOM is almost certainly heterogeneous, and the bulk <sup>14</sup>C value does not give a good idea of SOM dynamics. Even low-density organic matter is made up of relatively fresh litter material (small roots and pieces of leaves) as well as more humified materials that likely have slower turnover. Normally, the soil must be split into components with different turnover times using fractionation methods outlined in the text. For each component, a new measurement constraint (such as total C flux into and out of the soil) must be added to arrive at a unique solution. A second problem is that carbon entering the soil as litter may not have the <sup>14</sup>C signature of that year's atmospheric CO<sub>2</sub> (F<sub>atm</sub> in the equations above). For example, conifer needles often reside on trees for several years before they fall and are incorporated into soils. Failure to account for these time lags in living vegetation may result in an overestimate of the time required for decomposition (since the turnover time will reflect the time spent in the plant plus soil, rather than the soil alone).

### **Systems That Are Accumulating Carbon**

Again, net change in C storage (dC/dt) represents the balance between annual C inputs (I; kg C m<sup>-2</sup> y<sup>-1</sup>) and decomposition (kC, where k is a first-order decomposition rate constant (y<sup>-1</sup>), and C(t) is the organic layer C inventory kg C m<sup>-2</sup>) in year t. The solution to this (from above) is:

$$C(t) = \left(\frac{1}{k}\right)\left(1 - e^{-kt}\right) \tag{A11}$$

Using radiocarbon data to determine time, t, we can determine the history of C accumulation at a site. A plot of accumulated carbon inventory (C(t)) versus the time it took to accumulate (t, from radiocarbon) may then be fit with Equation (2) to derive estimates of I and k describing either decadal (bomb radiocarbon) or millennial (natural radiocarbon) C dynamics (Trumbore and Harden, 1997). An example is shown in Figure 10. Alternatively for a known-age disturbance or soil age, the amount of C accumulated, and the amount of radiocarbon accumulated, will uniquely determine I and k.



**Figure 10.** Accumulation of C in non-steady state soils from a mature black spruce/moss forested site in central Manitoba, Canada. Data shown are for Sphagnum moss that has accumulated since the site last burned ( $\sim$ 100 years before sampling) and for the humus and charred layer below the regrowing moss and including the A horizon. The soil is developed on the sediments of a lake that dried up  $\sim$ 7,000 years ago. The parameter I = plant input (kg C m<sup>-2</sup> y<sup>-1</sup>); k = decomposition constant (y<sup>-1</sup>).

#### Natural Radiocarbon

Prior to 1950, the  $^{14}$ C content of atmospheric CO<sub>2</sub> was approximately constant. For constant atmospheric  $^{14}$ C content ( $F_{atm} = 1.0$  pre-1960),  $F_{C}(t)$  may be expressed as:

$$F_C(t) = \frac{\frac{I}{(k+\lambda_{14})} \left[1 - e^{(-(k+\lambda_{14})t)}\right]}{C(t)}$$
(A12)

where t is the time since soil began to form. Substituting for C(t),

$$F_C(t) = \frac{k}{(k + \lambda_{14})} * \frac{\left[1 - e^{(-(k + \lambda_{14})t)}\right]}{\left[1 - e^{(-kt)}\right]}$$
(A13)

In their study of how different minerals affect the long-term turnover rates of carbon in soils of Hawaii, Torn et al. (1997) used measurements of Fc(t), and the known age of the ash deposit on which the soil was developed (t), together with Equation (12) to estimate the turnover time, 1/k.

#### Bomb Radiocarbon

To determine the inventory-weighted mean  $\Delta^{14}C$  value in 1996, we assume annual C additions are labeled with the  $\Delta^{14}C$  of that year's atmospheric CO<sub>2</sub>, and track the loss of C and  $^{14}C$  with time for each year's C input. Isotopes are assumed not to fractionate during decay (i.e., respired C is assumed to have the same  $^{14}C$  content as the organic matter in each annual layer). The equation expressing the inventory-weighted mean  $^{14}C$  content of the soil profile in year t after initiation of accumulation is:

$$F_{C}(t) = \frac{\sum_{i=0}^{i=T} C_{i}(t) F_{atm}(i)}{\sum_{i=0}^{i=T} C_{i}(t)}$$
(A14)

where T is the total number of years carbon has been accumulating (years since disturbance), and  $F_{atm}(i)$  is the Fraction Modern of C fixed in the year i (assumed to equal that year's atmospheric  $^{14}CO_2$ ), and Ci(t) = I/k (1-exp(-kt)) is the carbon remaining t years after it was fixed in year i (t = T - i). For example, consider a layer of moss and detritus sampled in 1994 that began to accumulate 120 years ago following a fire in a boreal forest. If the rate of C inputs is 120 g C m<sup>-2</sup> yr<sup>-1</sup>, and the decomposition rates is .02 yr<sup>-1</sup> (turnover time of 50 years), the total amount of carbon accumulated in 120 years will be 5.5 kg C m<sup>-2</sup>, and the bulk  $\Delta^{14}$ C of the moss layer will be +183 %. For the same input rate, but with faster decomposition (0.04 yr<sup>-1</sup>, or turnover time of 25 years), only 3.0 kg C m<sup>-2</sup> will have accumulated, with  $\Delta^{14}$ C of +231 %. Knowing the bulk amount of C and its inventory-weighted  $\Delta^{14}$ C value for a known period of accumulation will uniquely define I and k. Again, complications arise because of the assumption of zero time lag for C storage in vegetation (especially woody biomass that may represent a significant portion of the litter carbon in fire-dominated forest systems).

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